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(19)



(54) VULCANISATION AGENT

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to agents for use in the vulcanisation of rubbers and more particularly to compositions containing bis(thiophosphoryl)polysulphides.

Bis(dihydrocarbylthiophosphoryl)tri- and tetrasulphides are of value in the vulcanisation of rubbers as accelerators and, particularly, as replacements for all or part of the sulphur normally used. Benefits arising from the use of these compounds may include vulcanisates of increased stability to heat without increase in scorch or tendency to bloom and, in the case of rubber/polyester compositions improved heat stability of the polyester.

These bis(dihydrocarbylthiophosphoryl)tri- and tetrasulphides are conveniently prepared from dihydrocarbyldithiophosphoric acid and sulphur dichloride or sulphur monochloride respectively. However the products obtained, especially if technical qualities of sulphur chlorides are employed, are impure and purification procedures, such as recrystallisation or slurrying with a solvent lead not only to considerable losses but also to effluent problems in disposal of for example the solutions containing the impurities. It has now been found that the crude reaction product can be used as a vulcanisation agent instead of the purified tri- or tetrasulphide and affords vulcanisates with similar properties.

The impure products are not however entirely suitable for use in rubbers since they are usually obtained in the form of liquids or sticky solids which are difficult to handle, and it has been found that they may be adsorbed onto suitable adsorbents to give solid products which can be handled conveniently and in which the vulcanising

activity of the tri- or tetrasulphide has not been adversely affected.

According to the invention there is provided a composition comprising a crude bis(dihydrocarbylthiophosphoryl)tri- or tetrasulphide and a solid adsorbent as hereinafter defined.

As hydrocarbyl groups there are mentioned especially alkyl, cycloalkyl and aryl groups, it being preferred that they are all the same. The preferred hydrocarbyl groups are alkyl groups which may be primary, secondary or tertiary, and particularly alkyl groups containing from 1 to 9 carbon atoms, especially the ethyl group. As cycloalkyl groups there are mentioned cyclopentyl and cyclohexyl groups and as aryl groups there are mentioned phenyl and *o*-, *m*- and *p*-tolyl groups.

The words adsorb, adsorbing and adsorbent are not used in any restrictive sense but are intended to relate to the taking up of one substance by another without distinguishing whether the second substance is retained on the surface of, or completely permeates, the first substance.

The solid adsorbents suitable for use in the composition comprise highly adsorbent synthetic siliceous fillers and adsorbents. The naturally occurring siliceous fillers such as kieselguhr, Fuller's earth, talc, vermiculite and china clay suffer from the disadvantage of low adsorptive capacity and also in some cases give coloured products and are not suitable for use in the composition of the invention. The preferred siliceous fillers and adsorbents comprise:—

(1) highly adsorbent, synthetic, hydrated silicates of for example calcium, aluminium or magnesium, of fine particle size, by which is meant less than 0.1 μ , and low bulk density, by which is meant below 300 g./litre; and with moderate to high surface area, by which is meant more than 25 m²/g. As examples of such adsorbent silicates there may be mentioned those commercially available under the names of Calflo and Microcal (both calcium silicates) and Alusil (aluminum silicate) (Calflo, Microcal and Alusil are Registered Trade Marks).

[Price 33p]

(2) highly adsorbent synthetic amorphous silica of fine particle size, low bulk density and high surface area as defined above. As examples of such adsorbent silicas there may be mentioned those commercially available under the names of Aerosil, Manosil VN3, Santocel 54 and Santocel 62, Ultrasil and Wessalon (Aerosil, Manosil and Santocel are Registered Trade Marks).

Suitable amounts of the solid adsorbent are from 5 to 100% of the weight of impure tri- or tetrasulphide. It is usually preferred however to use from 10 to 50% since this range normally covers the minimum amounts of adsorbent which will give solid products which will flow readily and can be handled easily.

The impure tri- or tetrasulphide may be obtained for example by reacting at a suitable low temperature the dithiophosphoric acid and sulphur chloride either alone or, preferably, in an inert solvent such as petroleum ether or toluene, which solvent may be removed under reduced pressure. The residue is then mixed with the adsorbent in any conventional mixing or blending equipment, such as e.g., rotary mixers and blenders, horizontal mixers, vertical mixers and pan mixers and affords a composition suitable for use in the vulcanisation of rubbers. Suitable temperatures for the reaction lie within the range -50°C to the boiling point of the sulphur chloride being used or the boiling point of the solvent, whichever is the lower. Preferred temperatures are in the range -10°C to 30°C for sulphur dichloride and $+10^{\circ}\text{C}$ to 40°C for sulphur monochloride. Alternatively, a metal salt of the dithiophosphoric acid may be reacted with the sulphur chloride at a suitably low temperature, either alone, suspended or dissolved in an inert solvent, or in aqueous solution. In the first two cases the product is freed from inorganic salts by filtration, followed where necessary by evaporation of solvent, and is then mixed with the adsorbent. In the third case the product is separated from the aqueous solution, dried and is then mixed with the adsorbent.

If desired a conventional dedusting agent, such as a mineral oil, may be incorporated into the composition of the invention, preferably by addition to the adsorbent and the tri- or tetrasulphide when they are being mixed.

According to a further feature of the invention there is provided a process for the vulcanisation of rubber which comprises heating the rubber with a vulcanising amount of a composition comprising a crude bis(dihydrocarbylthiophosphoryl)tri- or tetrasulphide and a solid adsorbent as hereinbefore defined.

As rubbers there may be mentioned

natural rubber and synthetic rubbers, for example cis-polybutadiene, cis-polyisoprene, butadiene/methyl methacrylate copolymers, isobutane/diolefin copolymers, ethylene/propylene/diolefin terpolymers and other well-known types of sulphur vulcanisable synthetic rubbers.

The composition may be incorporated into the rubber before vulcanisation by any conventional procedure, for example on a two roll rubber mixing mill or in an internal mixer.

The vulcanisation is carried out in the same manner and, if desired, in the presence of the same additives, as for pure tri- or tetrasulphides, allowance being made for the content of tri- or tetrasulphide in the composition.

When used in absence of elemental sulphur or additional accelerator the composition should be employed in amount sufficient to provide tri- or tetrasulphide in amount between 1 and 10% and preferably between 2 and 5%, of the weight of rubber. Sulphur and/or additional accelerators in up to conventional amounts may also be present in which case the amount of tri- or tetrasulphide may be correspondingly reduced.

Other conventional adjuvants may also be present in the rubber before vulcanisation, for example zinc oxide, furnace and carbon blacks, fillers, antioxidants, antiozonants, peptisers, softening agents, blowing agents and pigments. The process is of especial value with rubber/polyester composite materials since the polyester in the vulcanisate has greater thermal stability than when conventional sulphur/accelerator systems are used.

Vulcanisation may be carried out at any convenient temperature but preferably between 100°C and 200°C .

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight unless otherwise stated.

Example 1

Diethyldithiophosphoric acid (103 parts) and petroleum ether (b.p. $40-60^{\circ}\text{C}$, 160 parts) are stirred at -10°C and sulphur dichloride (technical quality, 28.4 parts) is added dropwise over 2 hours keeping the temperature below 0°C . The mixture is stirred at -10°C to 0°C for 1 hour after the addition is complete and then allowed to warm up to room temperature. The petroleum ether is removed under reduced pressure on a rotary evaporator at a temperature below 40°C , leaving 106 parts of a light brown slightly sticky solid.

15 parts of this solid and 5 parts of a commercial calcium silicate are mixed by grinding in a mortar. The product is a white, slightly dusty powder.

Example 2

Diethyl dithiophosphoric acid (103 parts) and toluene (160 parts) are stirred at -10°C and sulphur dichloride (technical quality, 28.4 parts) is added dropwise over 2 hours keeping the temperature below 0°C . The mixture is stirred at -10°C to 0°C for 1 hour after the addition is complete. The solution is then stirred at room temperature and 10% aqueous caustic soda solution is added dropwise until the pH of the mixture becomes slightly alkaline. The aqueous layer is separated and the toluene layer washed twice with water. The toluene is removed by distillation under reduced pressure at $40-50^{\circ}\text{C}$. There remains 105 parts of a light brown, slightly sticky solid.

15 parts of this solid and 5 parts of a commercial calcium silicate are mixed by grinding in a mortar. The product is a white, slightly dusty powder.

Example 3

Diethyl dithiophosphoric acid (103 parts) and petroleum ether (b.p. $30-40^{\circ}\text{C}$, 160 parts) are cooled to -5°C in an ice-bath. Sulphur monochloride (technical quality, 37.1 parts) is added dropwise over 2 hours keeping the temperature below 20°C . The solution is then neutralised to pH 8 by the addition of 10% aqueous caustic soda solution. The aqueous layer is separated and the organic layer washed twice with water. The petroleum ether is then removed by distillation on a rotary evaporator under reduced pressure without the application of external heat leaving 108.5 parts of a light brown liquid product.

14 parts of this liquid and 6 parts of a commercial calcium silicate are mixed together by grinding in a mortar. The product is an off-white, free-flowing, non-dusty powder.

Example 4

The following rubber mixes are prepared on a two-roll laboratory rubber mill:

	A	B	C
Smoked Sheet Natural Rubber	100	100	100
Zinc oxide	3.5	3.5	3.5
Stearic acid	3.0	3.0	3.0
High Abrasion Furnace Black	45	45	45
Process Oil	3.5	3.5	3.5
Cyclohexylbenzthiazylsulphenamide	2	2	2
Bis(diethylthiophosphoryl)trisulphide	2	—	—
Product of Example 2	—	2.70	—
Product of Example 3	—	—	2.90

The weights taken of the products of Examples 2 and 3 are such as to give an organic material content of approximately two parts per hundred of rubber i.e. equivalent to the weight of pure bis(diethylthiophosphoryl)trisulphide taken in mix A.

To assess the curing activity of the

products of Examples 2 and 3 compared to the pure trisulphide, oscillating disc rheometer tests (a test widely used in the rubber industry for assessing the curing characteristics of compounds) are carried out at a temperature of 150°C with the results given in Table I.

TABLE I

Oscillating Disc Rheometer Results

Mix	A	B	C
Time to increase in torque of 4 in. lbs. (mins.) (A guide to the processing safety of the compounds)	6.8	6.8	5.7
Time to 95% cross-linking (mins.) (Taken as a guide to optimum cure)	17	17	13.5
Peak Torque Value (in. lbs.) (A guide to the modulus and hence state of cure of the compound)	37	37	45

It is clear from these results that the products of Examples 2 and 3 are as active as the pure trisulphide.

5 Samples of the above mixes in the form of sheets 0.8 mm thick are vulcanised in a press

for 20 minutes at 153° C. Oxygen Absorption measurements at 100° C are then made on these vulcanisates to assess their resistance to oxidative degradation. Results are given in Table II.

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TABLE II

Oxygen Absorption Results

	A	B	C
Time (hours) to 1% w/w oxygen absorption	48	48	44

15 The results indicate that there is no significant difference between the vulcanisates in their resistance to oxidative degradation.

Example 5

Diethyldithiophosphoric acid (412 parts) and toluene (320 parts) are stirred at room temperature and sulphur dichloride (120 parts of technical quality material) is run in dropwise keeping the temperature below 25° C. The mixture is then stirred for a further hour at room temperature. Aqueous caustic liquor (10 % w/v) is then run in until the pH of the mixture lies between 8 and 9. The aqueous layer is discarded and the toluene layer is washed twice with water. The toluene is evaporated off on a rotary evaporator under reduced pressure at a temperature not exceeding 65° C. There remains 386 parts of a light brown partially crystalline material.

32 parts of this material is blended thoroughly with 8 parts of a commercial, finely divided amorphous hydrated silica. The product is an off-white, slightly dusty powder.

Example 6

80 parts of the partially crystalline material of Example 5 is blended thoroughly with 17 parts of a commercial, finely divided, amorphous, hydrated silica and 3 parts of a mineral oil as dedusting agent. The product is an off-white, free-flowing non-dusting powder.

Example 7

Diethyl dithiophosphoric acid (103 parts) is stirred and a solution of caustic soda (20 parts) in water (80 parts) is added dropwise keeping the temperature below 25° C. The resulting aqueous solution of the sodium salt is separated from a small amount of undissolved material and is cooled to 0° C. Sulphur dichloride (28.4 parts) is added dropwise keeping the temperature below 10° C. A sticky solid separates out from solution. After a further 30 minutes stirring the pH of the mixture is adjusted to 8—9 by the addition of aqueous caustic soda. The aqueous solution is decanted off from the sticky solid, which is washed thoroughly with water and is then dried below 60° C. It amounts to 85.6 parts.

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32 parts of the solid are blended thoroughly with 8 parts of a commercially available finely divided amorphous hydrated silica. The product is a white slightly dusty powder.

Example 8

693 parts of a technical grade of the sodium salt of diethyl dithiophosphoric acid bulked with sodium carbonate and having an active agent content of 60 % is slurried in 320 parts of toluene. 136 parts of technical sulphur dichloride is added dropwise keeping the temperature below 25° C, and the mixture is stirred for 1 hour at room temperature after completion of the addition. The toluene solution is filtered free of inorganic matter and the filter cake is washed with more toluene. The toluene solution and washings are evaporated under reduced pressure below 65° C. The residual partially crystalline mass amounts to 374 parts. This material is intimately blended with 93.5 parts of a commercially available finely divided amorphous hydrated silica. The product is an off-white slightly dusty powder.

Example 9

78.7 parts of a technical grade of the sodium salt of diisopropyl dithiophosphoric acid bulked with sodium carbonate having an active agent content of 60 % is slurried in 80 parts of toluene. 13.2 parts of technical sulphur dichloride is run in dropwise keeping the temperature below 25° C and stirring is continued for a further hour after the addition is complete. The toluene solution is filtered free of inorganic matter and the filter cake is washed with more toluene. The toluene solution and washings are evaporated under reduced pressure keeping the temperature below 65° C. The residual liquid amounts to 44.5 parts. 29 parts of the liquid are mixed intimately with 11 parts of a commercially available finely divided

amorphous hydrated silica. The product is an off-white free-flowing powder.

Example 10

Dibutyl dithiophosphoric acid (48.4 parts) and toluene (40 parts) are stirred at 0° C and sulphur dichloride (10.8 parts of technical quality material) is run in dropwise keeping the temperature below 10° C. The mixture is allowed to warm up to room temperature and the pH is adjusted to between 8 and 9 by the addition of aqueous caustic soda solution. The toluene layer is separated off and washed twice with water. The toluene is then evaporated off below 65° C under reduced pressure to give 48.5 parts of a golden yellow oil. 28.5 parts of this oil are blended intimately with 9.5 parts of a commercially available finely divided amorphous hydrated silica. The product is an off-white free-flowing powder.

Example 11

Dibutyl dithiophosphoric acid (48.4 parts) and toluene (40 parts) are stirred together at 0° C and sulphur monochloride (14.8 parts of technical quality material) is run in dropwise keeping the temperature below 10° C. The mixture is allowed to warm up to room temperature and the pH is adjusted to between 8 and 9 by the addition of aqueous caustic soda solution. The toluene layer is separated off and washed twice with water. The toluene is then evaporated off under reduced pressure at a temperature not exceeding 65° C, giving 53.0 parts of a golden yellow oil. 33 parts of this oil are blended intimately with 11 parts of a commercially available finely divided amorphous hydrated silica. The product is an off-white free-flowing powder.

Example 12

Rubber mixes containing the products of Example 5 and Examples 7 to 11 were prepared and tested as described in Example 4. The results obtained are given below.

Smoked Sheet Natural Rubber	100						
Zinc oxide	3.5						
Stearic acid	3.0						
High Abrasion Furnace Black	45.0						
Processing Oil	3.5						
Cyclohexyl benzthiazyl sulphenamide	2.0						
bis(diethylthiophosphoryl)trisulphide	2.0						
Product of Example 5		2.5					
" " " 7			2.5				
" " " 8				2.5			
" " " 9					2.76		
" " " 10						2.67	
" " " 11							2.67

Oscillating Disc

Rheometer 150°C

Time to increase in torque of 4 in. lbs. (mins.)	6.3	5.9	5.7	5.7	6.9	8.0	6.1
Time to 95% cross linking (mins.)	16	15	13	15	19	20	16
Peak Torque (in. lbs.)	43	43	43	46	43	39	36

Oxygen Absorption at 100°C

Time to 1% Uptake (hours)	50	46	45	45	39	45	68
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WHAT WE CLAIM IS:—

1. A composition comprising a crude bis(dihydrocarbylthiophosphoryl tri- or tetra-sulphide and a solid adsorbent which is a highly adsorbent synthetic siliceous filler or adsorbent of particle size less than 0.1μ , bulk density below 300 g./litre and surface area more than 25 m²/g.
2. A composition as claimed in Claim 1 wherein the adsorbent is a highly adsorbent, synthetic, hydrated silicate of calcium, aluminium or magnesium.
3. A composition as claimed in Claim 1 wherein the adsorbent is a highly adsorbent amorphous silica.
4. A composition as claimed in Claims 1—3 wherein the amount of adsorbent is from 5 to 100% of the weight of crude bis(dihydrocarbylthiophosphoryl)tri- or tetra-sulphide.
5. A composition as claimed in Claims 1—3 wherein the amount of adsorbent is from 10 to 50% of the weight of crude bis(dihydrocarbylthiophosphoryl)tri- or tetra-sulphide.
6. A composition as claimed in Claims 1—5 wherein the hydrocarbyl group is an alkyl group containing from 1 to 9 carbon atoms.
7. A composition as claimed in Claims 1—6 wherein the hydrocarbyl group is an ethyl group.
8. A composition as claimed in Claims 1—7, which contains a dedusting agent.
9. A composition as claimed in Claim 1 substantially as hereinbefore particularly described.
10. A process for the vulcanisation of rubber which comprises heating the rubber with a vulcanising amount of a composition claimed in Claims 1—9.
11. A process as claimed in Claim 10

wherein the weight of tri- or tetrasulphide in the vulcanising amount is between 1 and 10% of the weight of rubber.

12. A process as claimed in Claim 10 wherein the weight of tri- or tetrasulphide in the vulcanising amount is between 2 and 5% of the weight of rubber.

13. A rubber vulcanisate whenever prepared by a process claimed in Claims 10—12.

14. A rubber/polyester composite in which the rubber has been vulcanised by a process claimed in Claims 10—12.

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Reference has been directed in pursuance of section 9, subsection (1) of the Patents Act, 1949, to patent No. 1,271,224.

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